

# Evaluating the protection of US EPA water quality criteria for copper or ammonia to freshwater mussels

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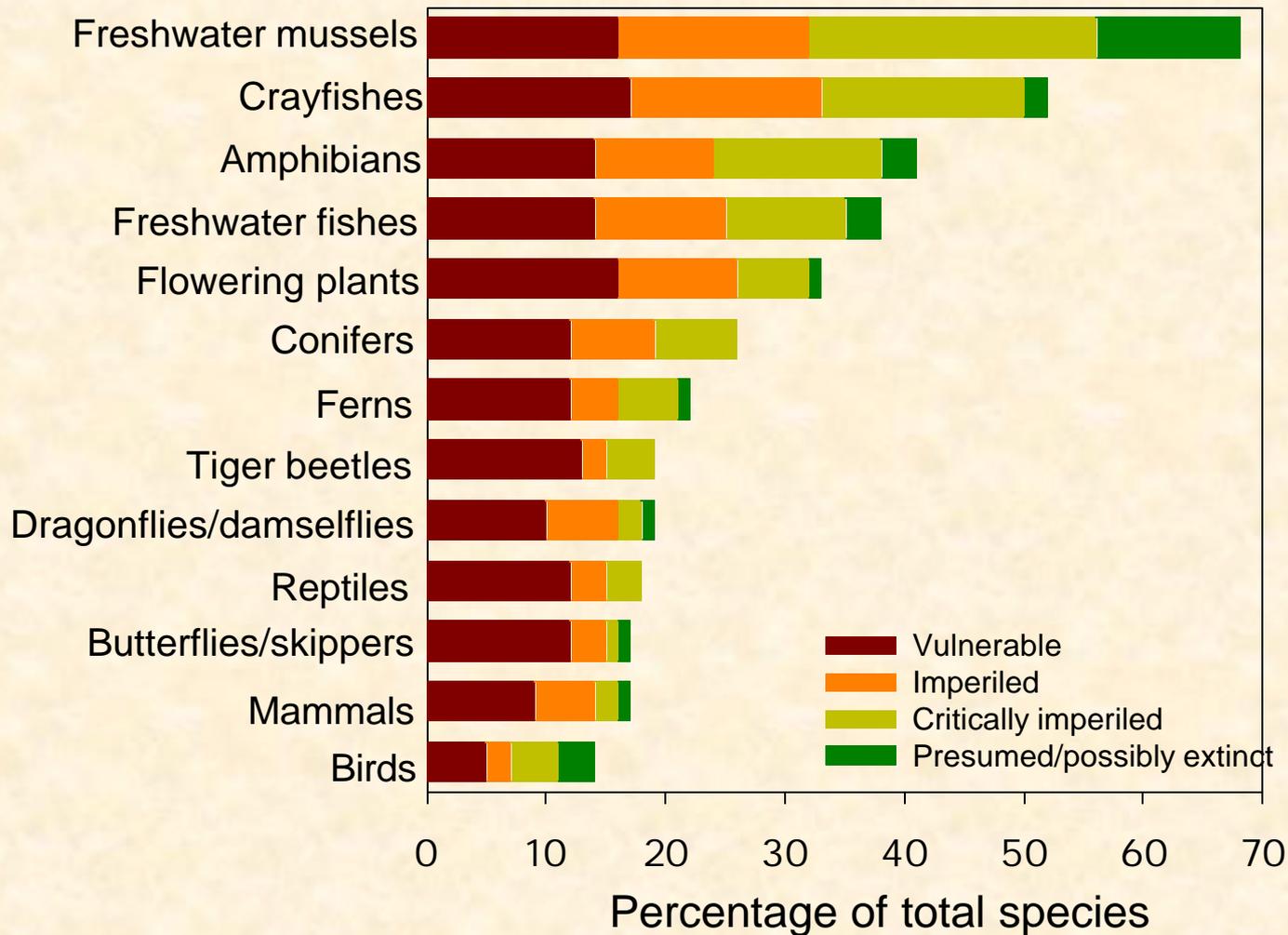
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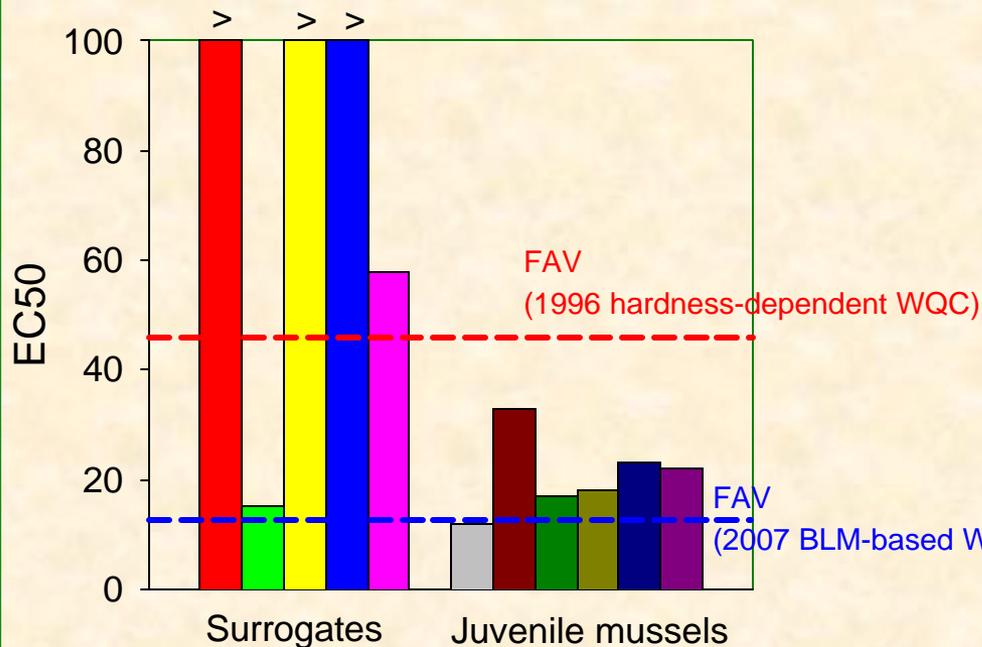
# Organisms listed as vulnerable, imperiled, or extinct in the United States



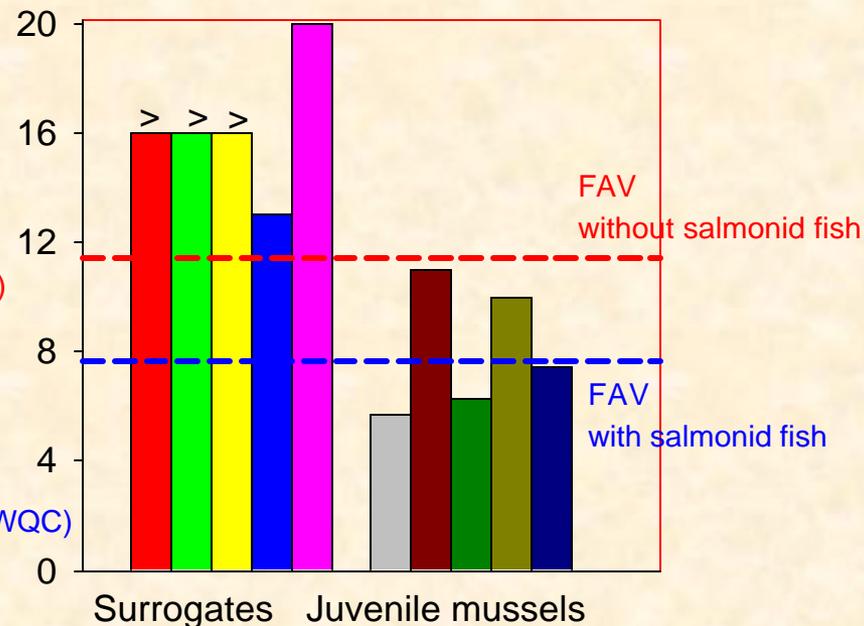
Stein et al. 2000

# 96-h EC50s of copper or ammonia for newly transformed mussels, compared to 48- or 96-h EC50s for surrogate species

Copper (ug/L)



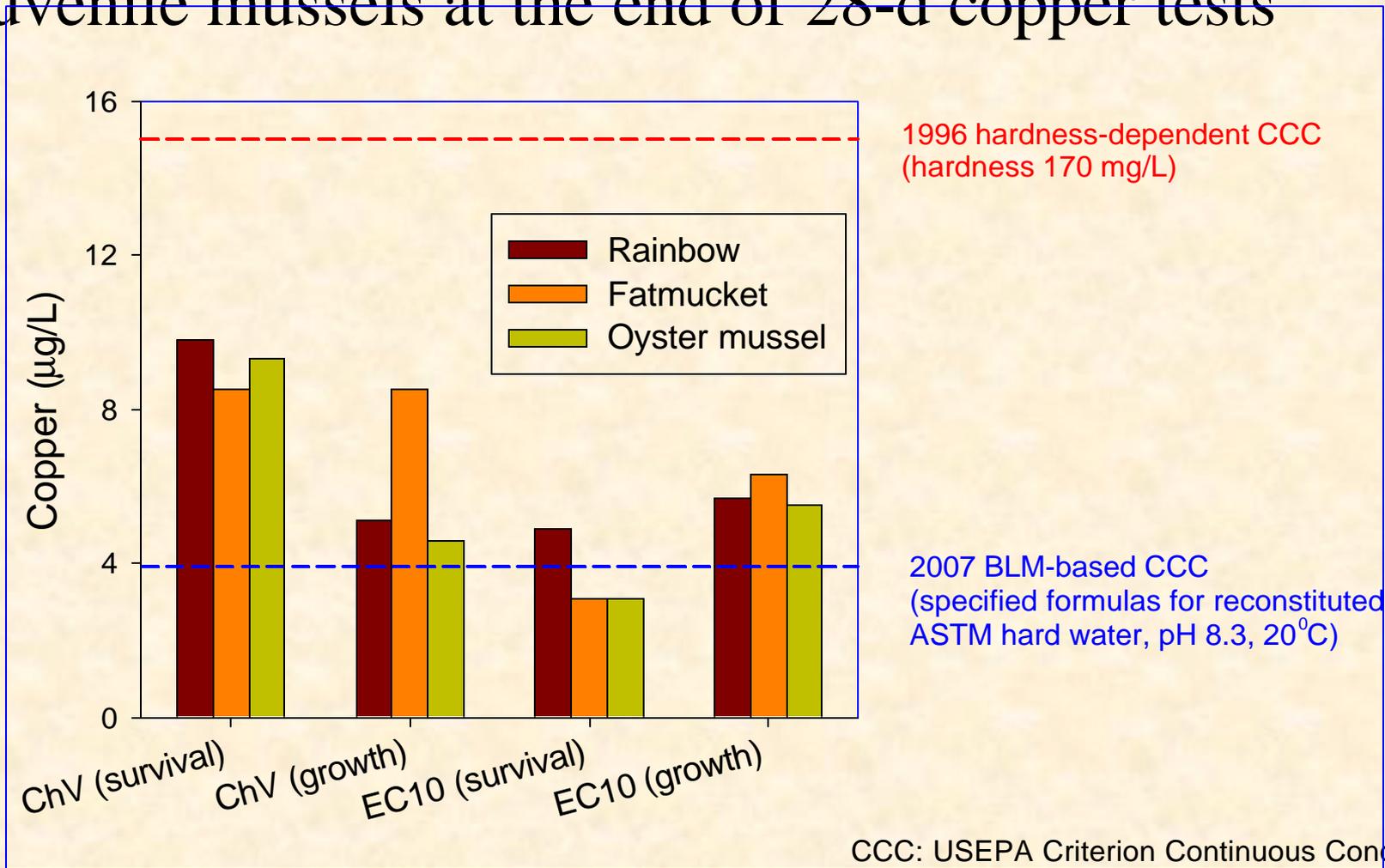
Total ammonia (mg N/L)



- |  |   |
|--|---|
| <span style="color: red;">█</span> <i>Daphnia magna</i>        | <span style="color: lightgrey;">█</span> Oyster mussel (Federal endangered sepcies) |
| <span style="color: green;">█</span> <i>Ceriodaphnia dubia</i> | <span style="color: brown;">█</span> Neosho mucket                                  |
| <span style="color: yellow;">█</span> <i>Hyalella azteca</i>   | <span style="color: green;">█</span> Rainbow  |
| <span style="color: blue;">█</span> Fathead minnow             | <span style="color: olive;">█</span> Fatmucket                                      |
| <span style="color: magenta;">█</span> Rainbow trout           | <span style="color: darkblue;">█</span> Wavy-rayed lampmussel                       |
|  | <span style="color: purple;">█</span> Scaleshell (Federal endangered sepcies)       |

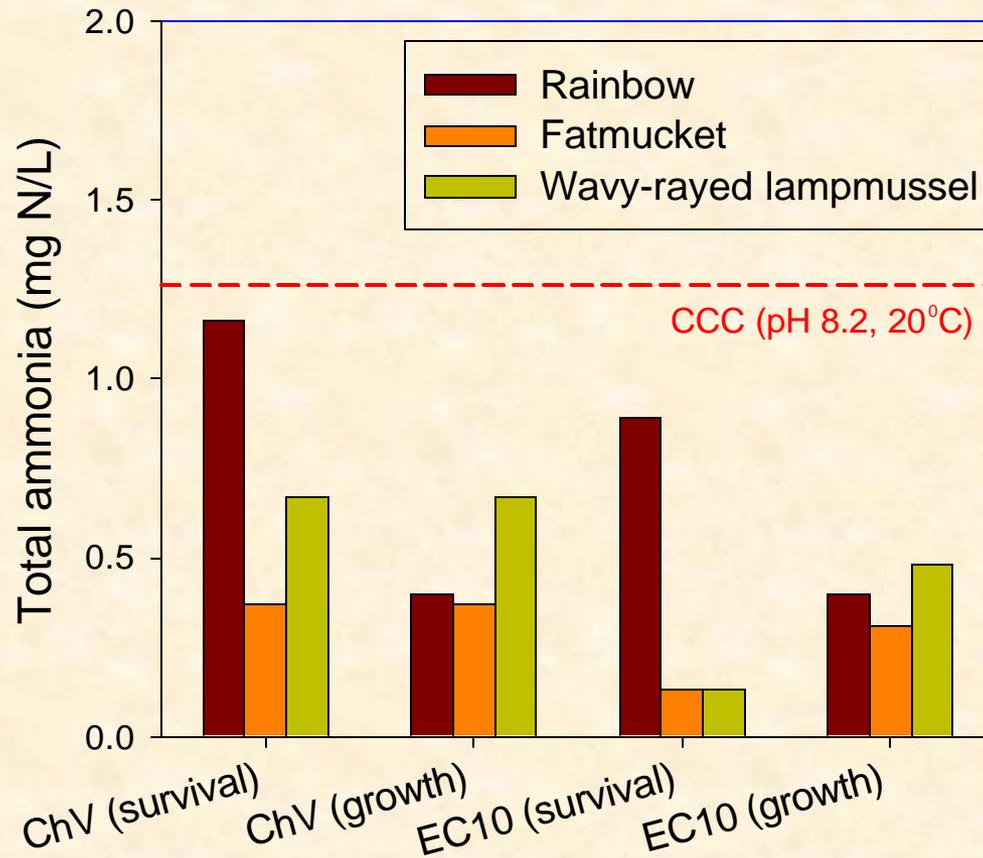
FAV: Final acute value for ASTM hard water (e.g., hardness 170 mg/L, pH 8.2)

# Chronic values and EC10 for survival and growth of juvenile mussels at the end of 28-d copper tests



Wang et al. 2007

# Chronic values and EC10 for survival and growth of juvenile mussels at the end of 28-d ammonia tests



CCC: USEPA Criterion Continuous Concentration

# Study questions

- Is the toxicity of copper or ammonia to mussels affected by water quality characteristics (e.g., DOC, pH)?
- Can the model in current USEPA WQC predict the toxicity of copper or ammonia to freshwater mussels?
- Are USEPA WQC for copper or ammonia adequately protective to freshwater mussels?

# Conditions for copper toxicity test with juvenile mussels in various natural and reconstituted waters (ASTM 2008)

**Test chemical:** Copper sulfate

**Test type:** Static-renewal

**Test duration:** 96 h

**Temperature:** 20±1°C

**Renewal of solution:** After 48 h

**Age of organism:** ~10 d

**Number of organisms/chamber:** 5

**Number of replicates/concentration:** 4

**Dilution water:** Reconstituted waters with similar anions, cations, and pH to nature waters

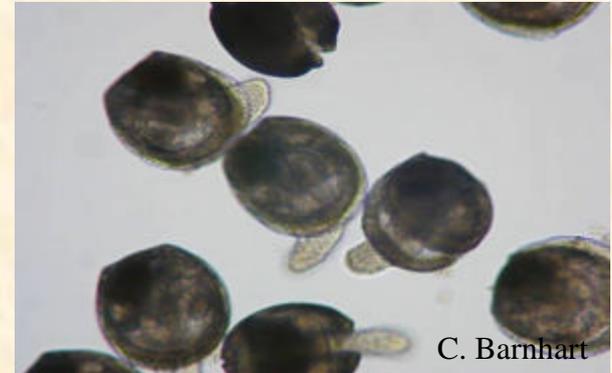
**Dilution:** Control and 5 copper concentrations

- 4 DOC levels: 0, 2.5, 5, and 10 mg C/L

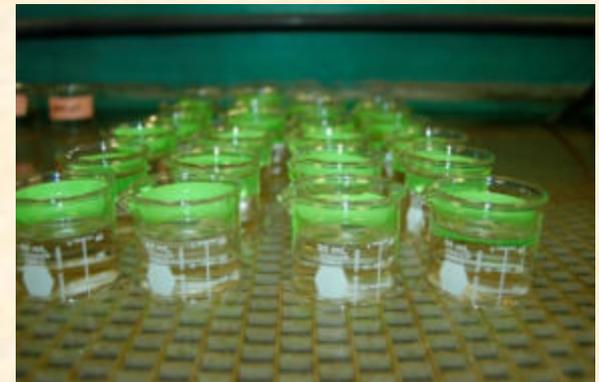
- 4 hardness: ASTM soft to very hard water

**Endpoint:** Survival (foot movement)

**Acceptability:** =90% survival in control



Test species: Fatmucket  
(*Lampsilis siliquoidea*)



Test chamber: 50-ml glass beaker with 30 ml of solution

## Water quality characteristics in natural and reconstituted waters

Water	DOC		Conductivity ( $\mu\text{S/cm}$ )	Hardness ( $\text{mg CaCO}_3/\text{L}$ )	Alkalinity	Ammonia ( $\text{mg N/L}$ )	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	Dissolved Cu ( $\mu\text{g/L}$ )
	( $\text{mg C/L}$ )	pH											
<b>Pond (P)</b>	<b>10.8</b>	<b>8.2</b>	<b>351</b>	<b>132</b>	<b>138</b>	<b>0.1</b>	<b>31</b>	<b>12</b>	<b>20</b>	<b>4.8</b>	<b>11</b>	<b>21</b>	<b>1.7</b>
P-dilution water	0.9	8.2	348	130	120	0.1	32	12	19	1.3	25	26	0.4
<b>Eagle Bluffs (EB)</b>	<b>9.5</b>	<b>8.5</b>	<b>1355</b>	<b>172</b>	<b>150</b>	<b>0.6</b>	<b>48</b>	<b>17</b>	<b>173</b>	<b>28</b>	<b>102</b>	<b>289</b>	<b>1.8</b>
EB-dilution water	0.9	8.5	1451	182	161	0.1	53	16	183	42	87	302	0.5
<b>Ditch #6 (D6)</b>	<b>9.8</b>	<b>7.9</b>	<b>110</b>	<b>42</b>	<b>40</b>	<b>0.2</b>	<b>11</b>	<b>5.0</b>	<b>3.9</b>	<b>1.5</b>	<b>4.9</b>	<b>4.8</b>	<b>1.1</b>
D6-dilution water	0.8	7.9	117	42	40	0.1	16	3.6	2.6	2.6	9.8	5.2	0.1
<b>Luther Marsh</b>	<b>10.5</b>	<b>8.4</b>	<b>602</b>	<b>200</b>	<b>126</b>	<b>0.4</b>	<b>76</b>	<b>40</b>	<b>341</b>	<b>42</b>	<b>192</b>	<b>5.7</b>	<b>1.5</b>
<b>ASTM hard</b>	<b>0.3</b>	<b>8.3-8.6</b>	<b>550-590</b>	<b>160-180</b>	<b>110-120</b>	<b>0.1-0.2</b>	<b>31</b>	<b>21</b>	<b>51</b>	<b>4.5</b>	<b>188</b>	<b>6.2</b>	<b>0.7-0.8</b>

Sigma-Aldrich humic acid was also used to prepare DOC water for test  
 - adding humic acid sodium salt into ASTM hard water

# Conditions for ammonia toxicity tests with juvenile mussels at five pH levels (ASTM 2008)



Diluter system with pH control system

**Test species:** Fatmucket (*L. siliquoidea*)

**Test chemical:** Ammonium chloride

**Test type:** Flow-through

**Test duration:** 96 h

**Temperature:** 20±1°C

**Age of organism:** ~10 d

**Number of organisms/chamber:** 10

**Number of replicates/concentration:** 3

**Test solution volume:** 200 ml

**Addition of solution:** 125 ml/4 h

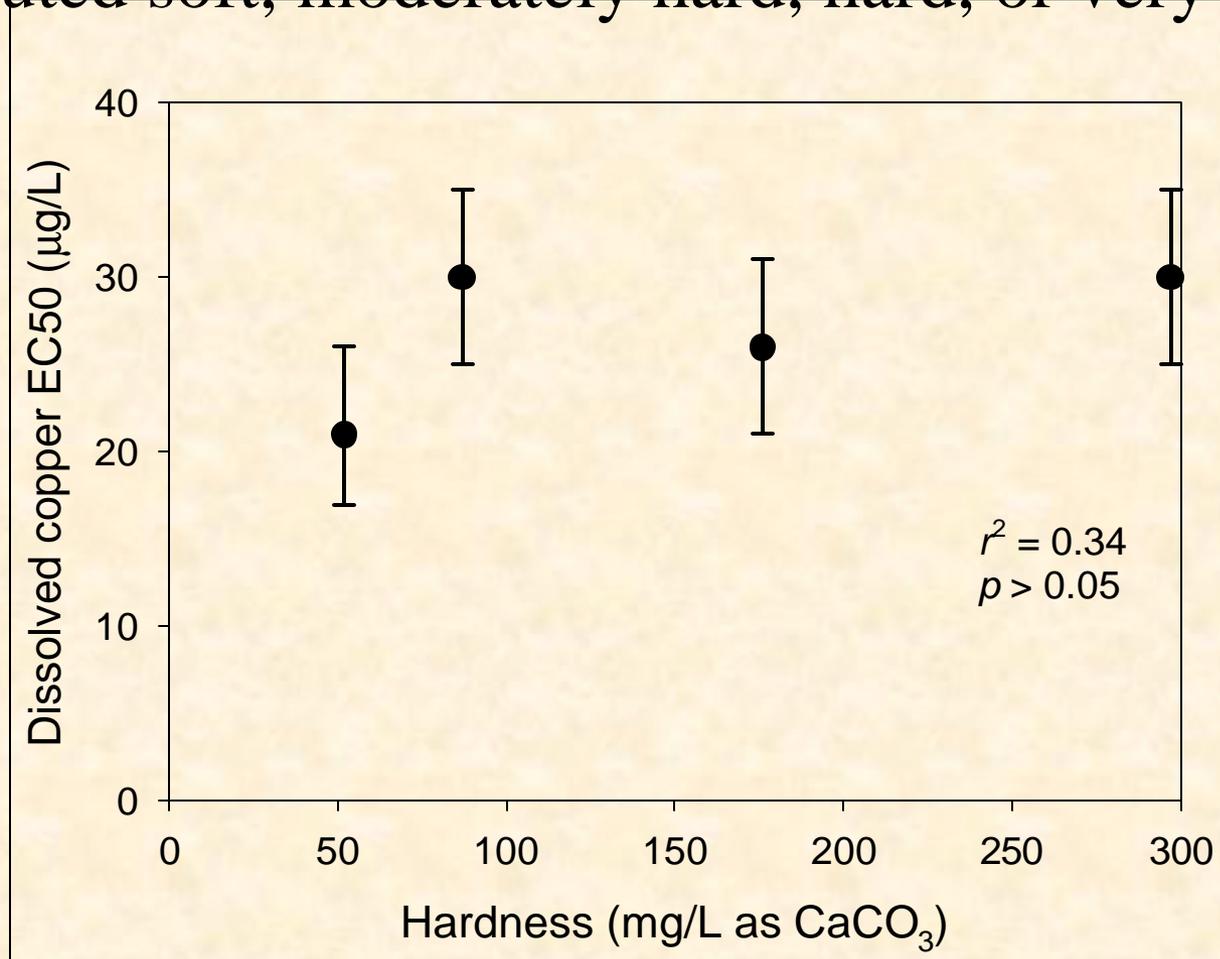
**Dilution water:** ASTM hard water

**Dilution:** Control and 5 ammonia concentrations at each of 5 pH levels (6.5, 7.5, 8.0, 8.5, and 9.0)

**Endpoint:** Survival (foot movement)

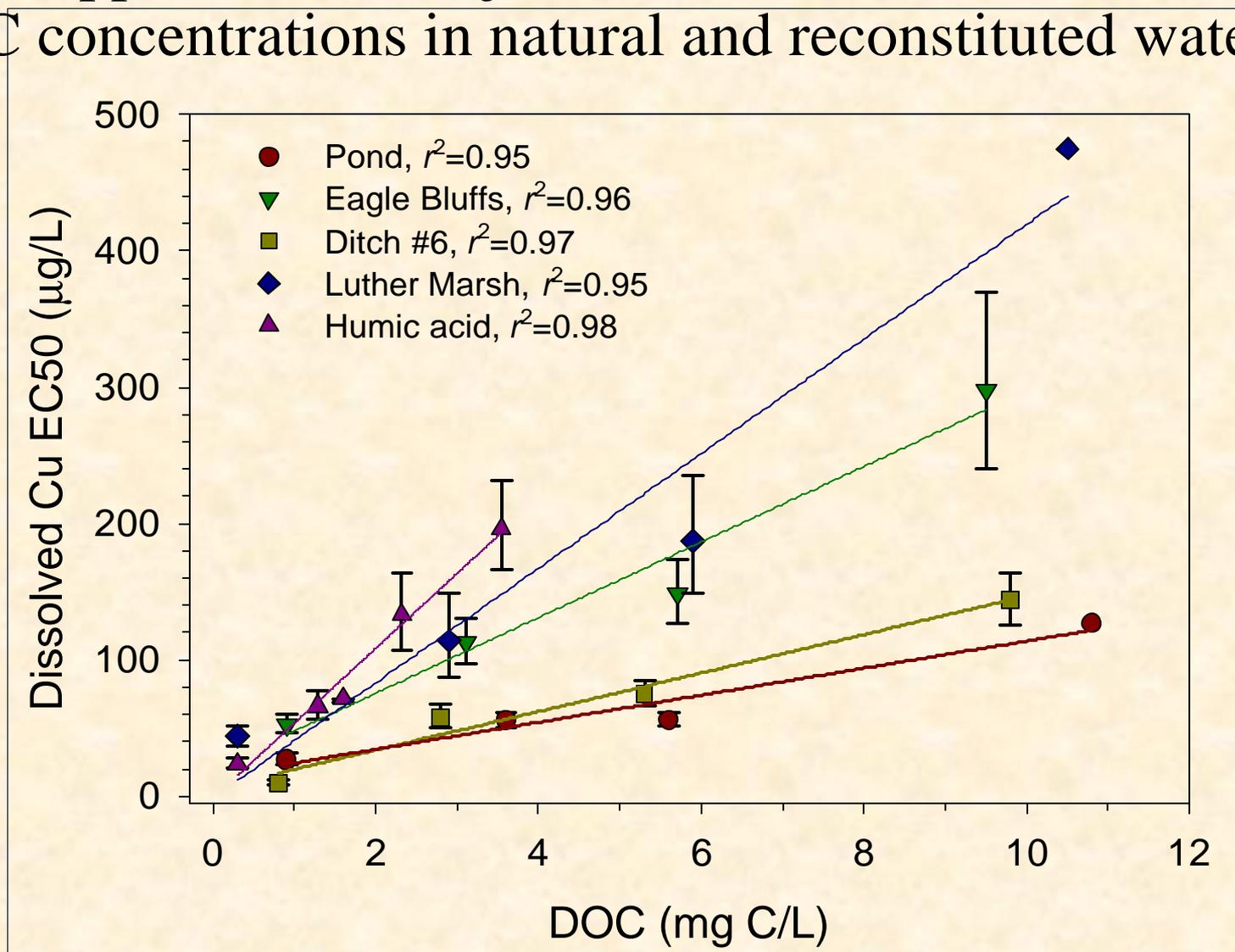
**Acceptability:** =90% survival in control

# 96-h copper EC50 for juvenile fatmucket in ASTM reconstituted soft, moderately hard, hard, or very hard water



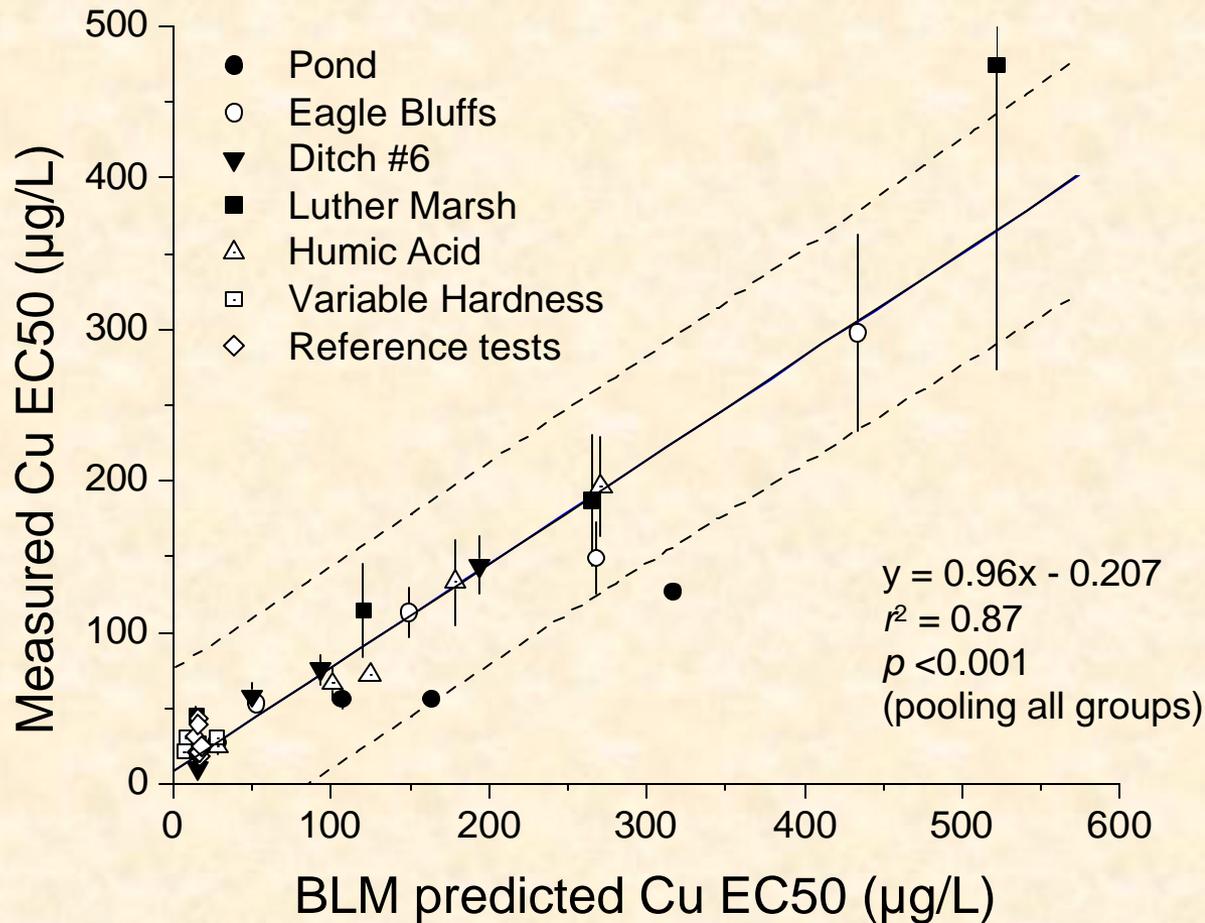
Error bar: 95% confidence interval

# 96-h copper EC50s for juvenile fatmucket at different DOC concentrations in natural and reconstituted waters



Error bar: 95% confidence interval

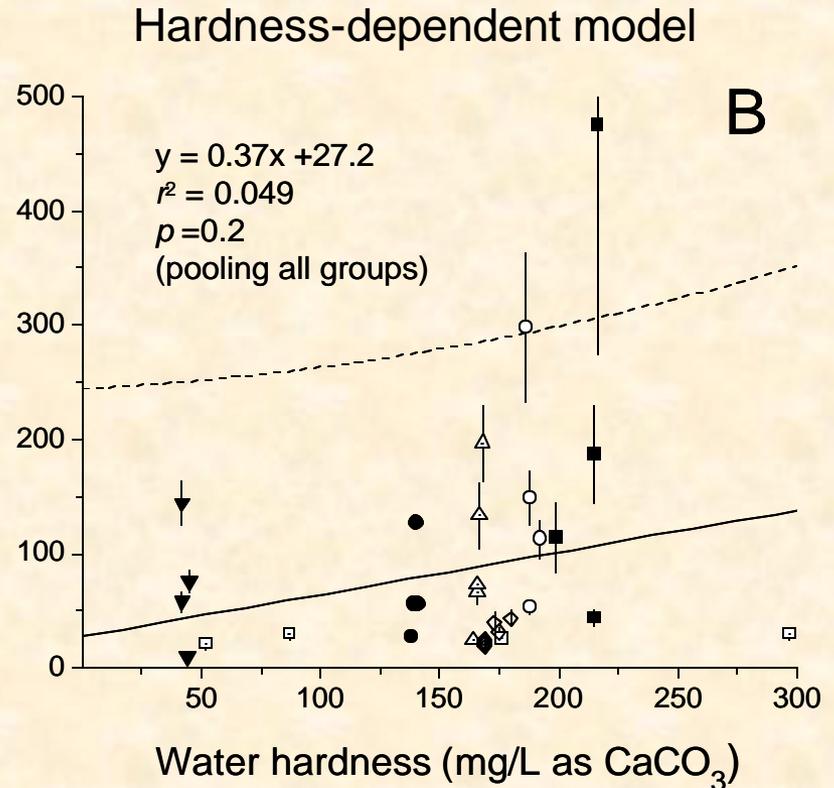
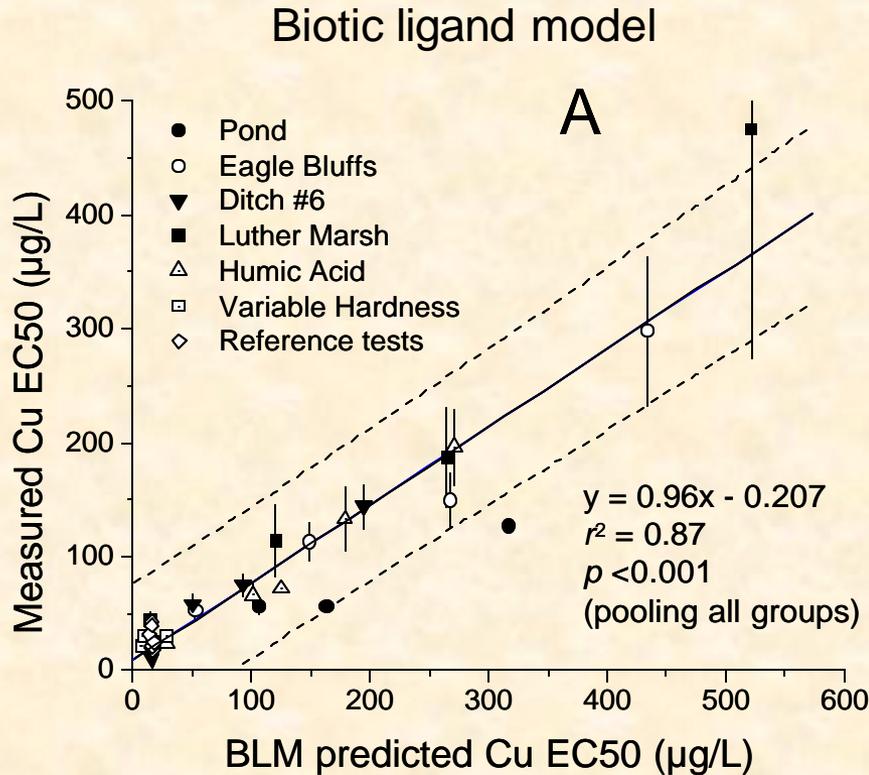
# Predictions of copper EC50s for juvenile fatmucket using biotic ligand model (HydroQual 2007, USEPA 2007)



Error bar: 95% confidence interval

Dashed lines: 95th percentile prediction band for EC50s

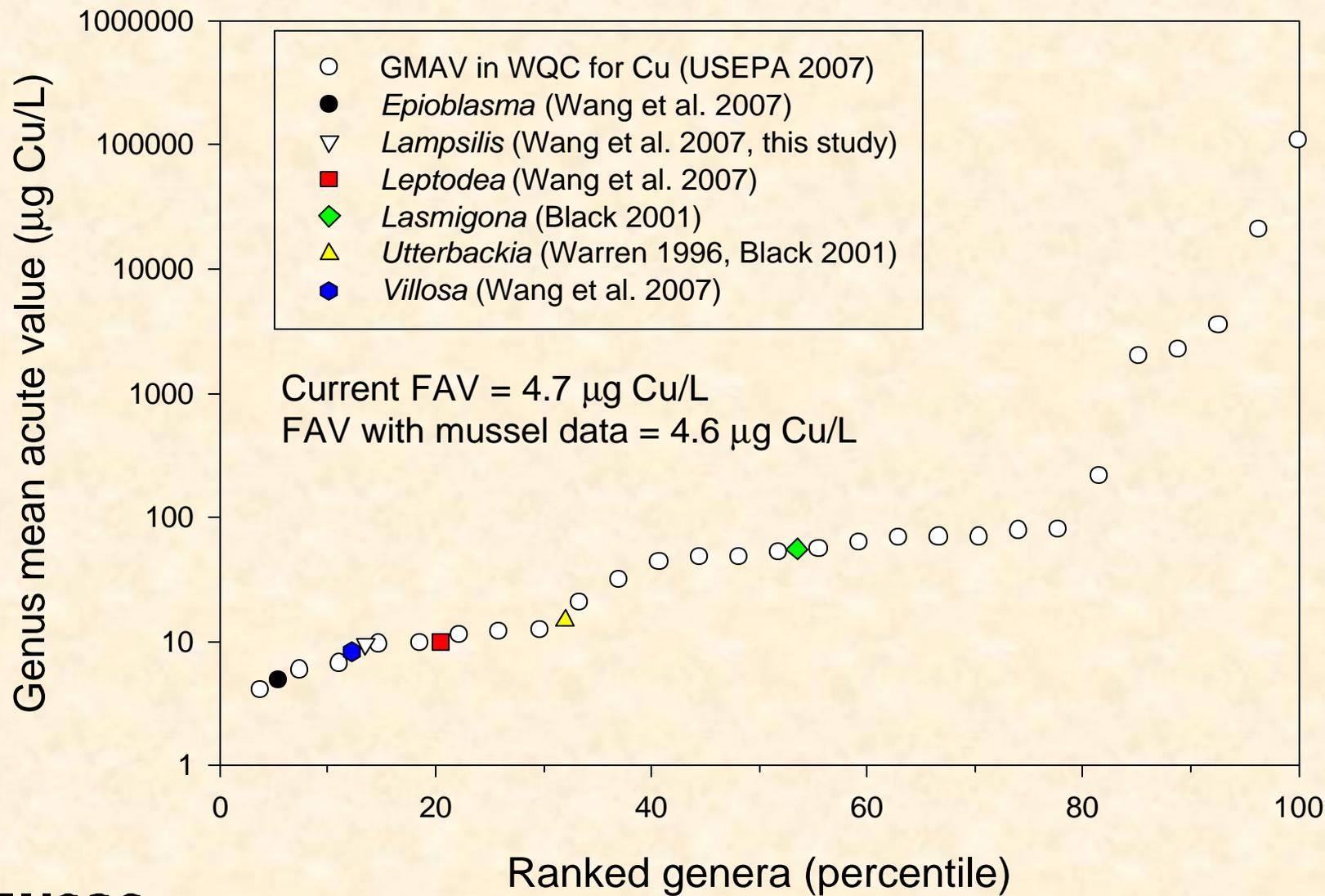
# Predictions of copper EC50s for juvenile mussels fatmucket: BLM vs. hardness-dependent model prediction



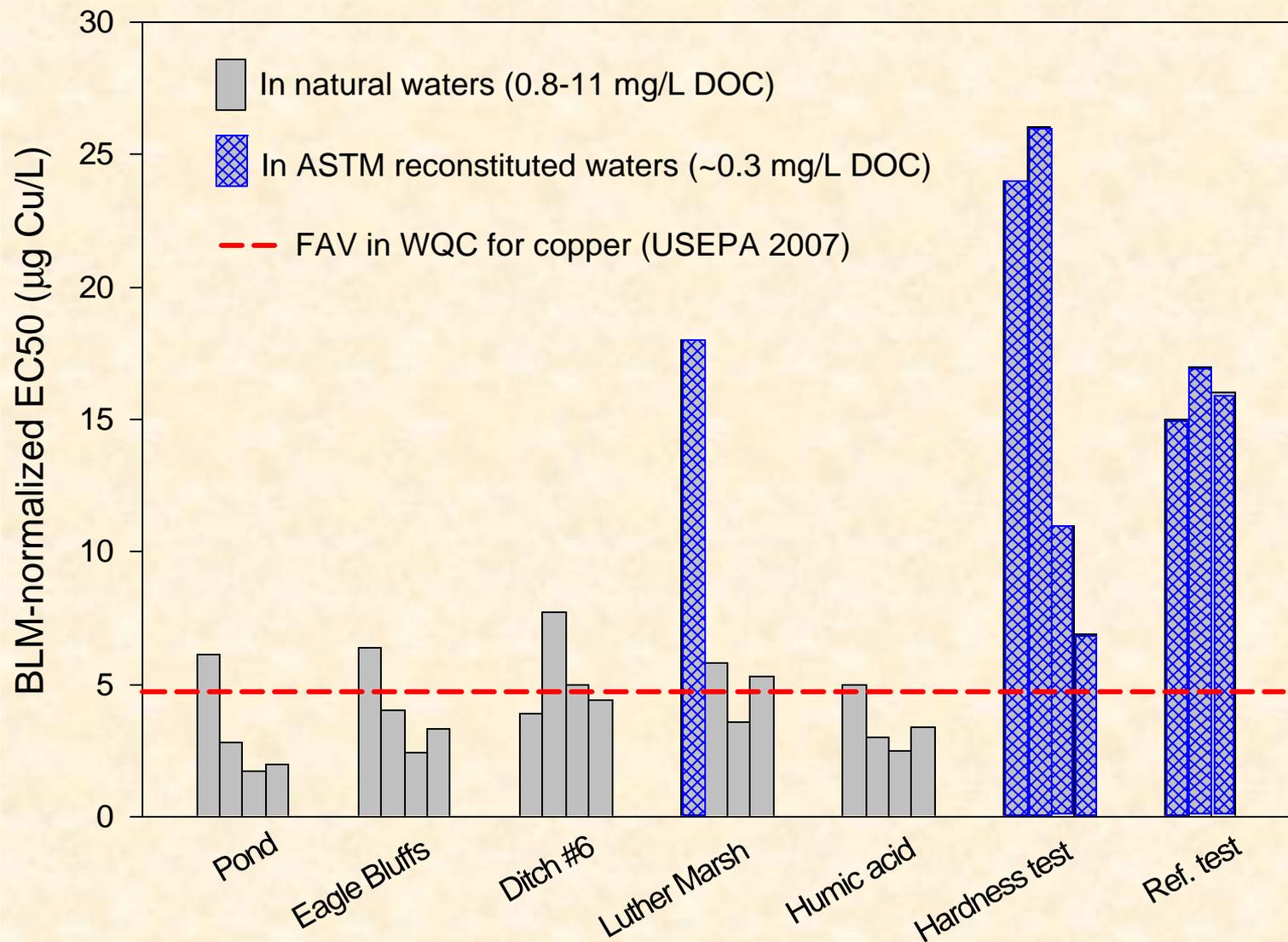
Error bar: 95% confidence interval

Dashed lines: 95th percentile prediction band for EC50s

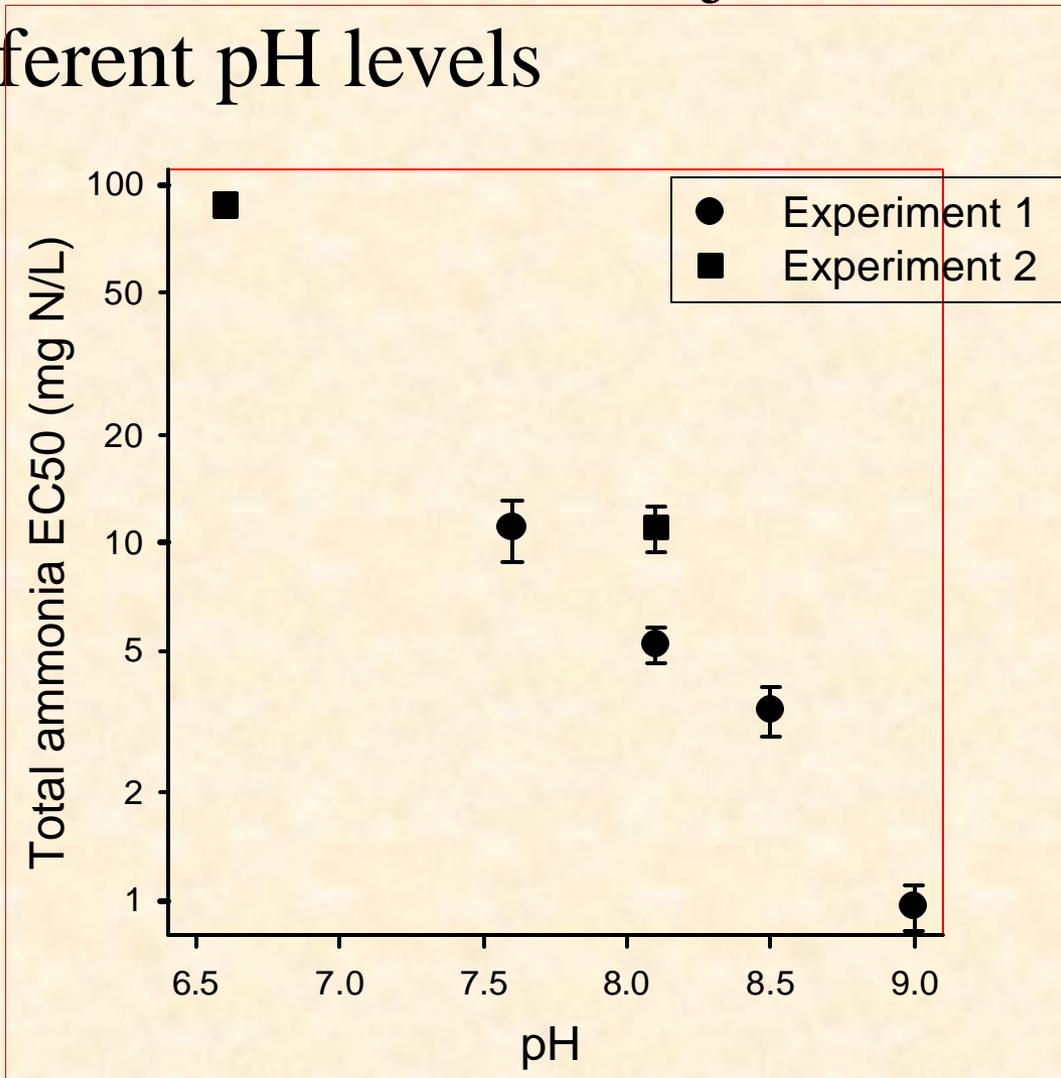
# Ranked genus mean acute values (GMAVs) in the USEPA water quality criteria for copper, with six GMAVs for mussels



# BLM-normalized EC50 for juvenile fatmucket in natural and reconstituted ASTM waters (this study)

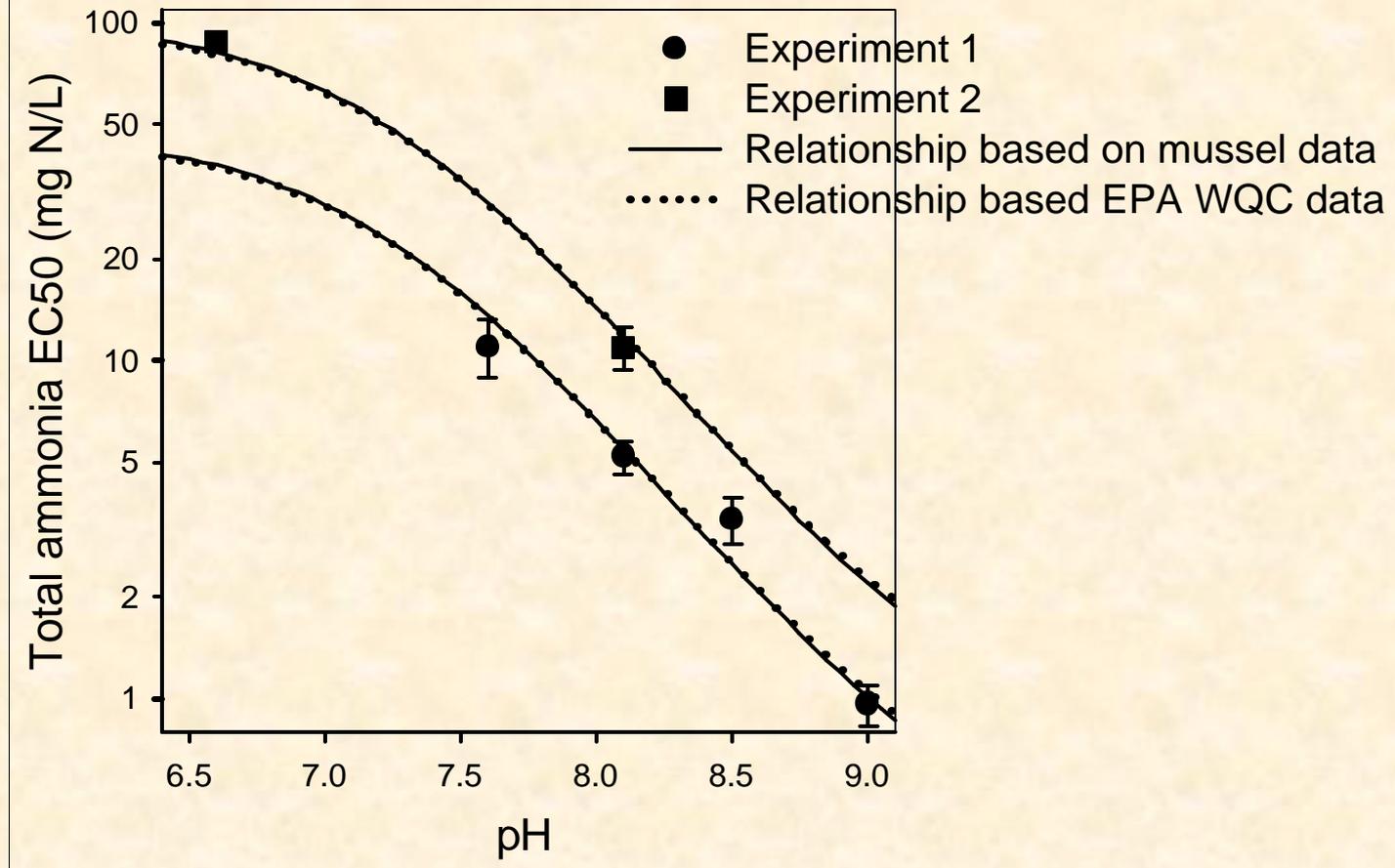


# 96-h ammonia EC50s for juvenile fatmucket at different pH levels



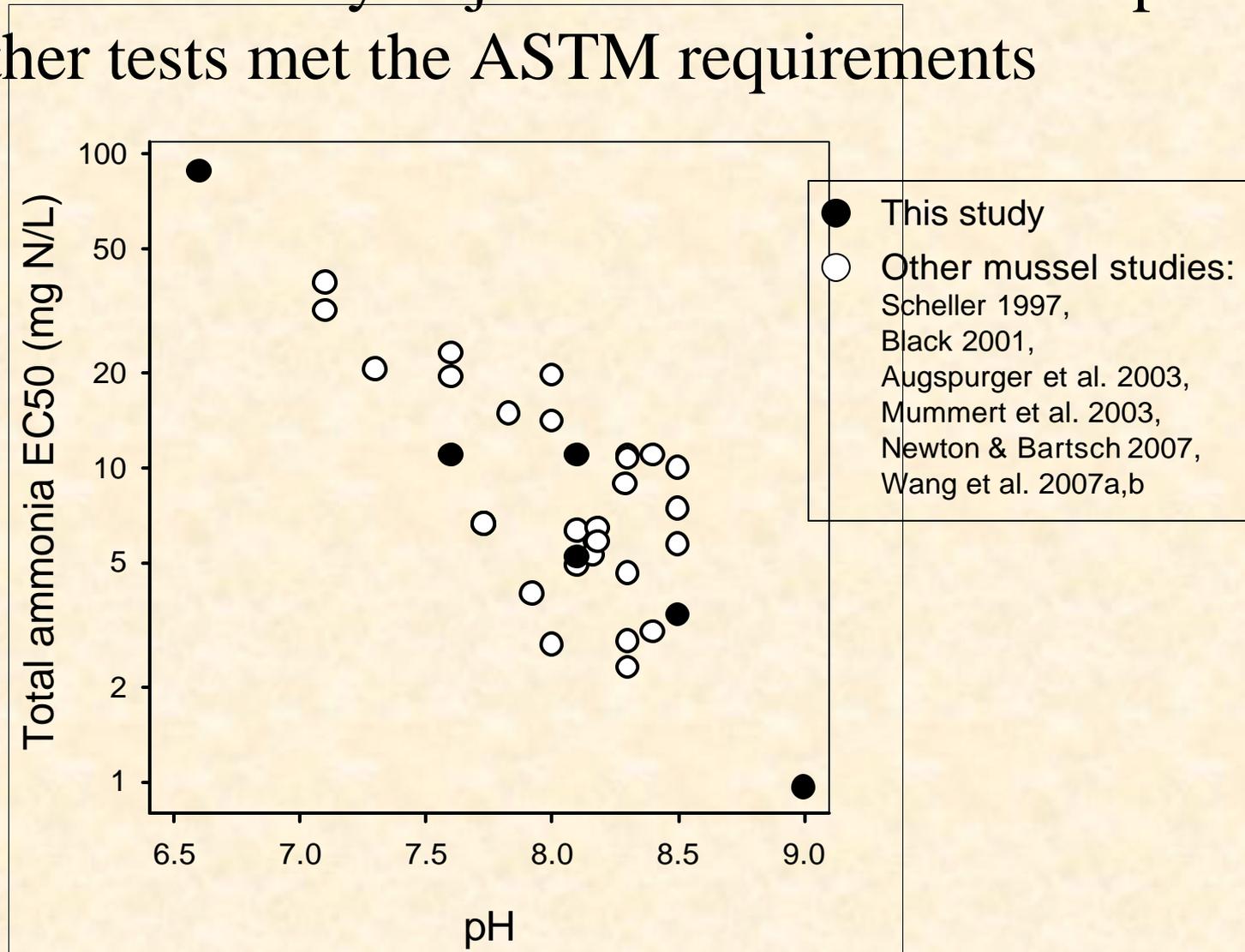
Error bar: 95% confidence interval

EC50 versus pH relationships for the mussel test or for pooled data in EPA WQC for ammonia, fitted to coincide with the same EC50s at pH 8.0

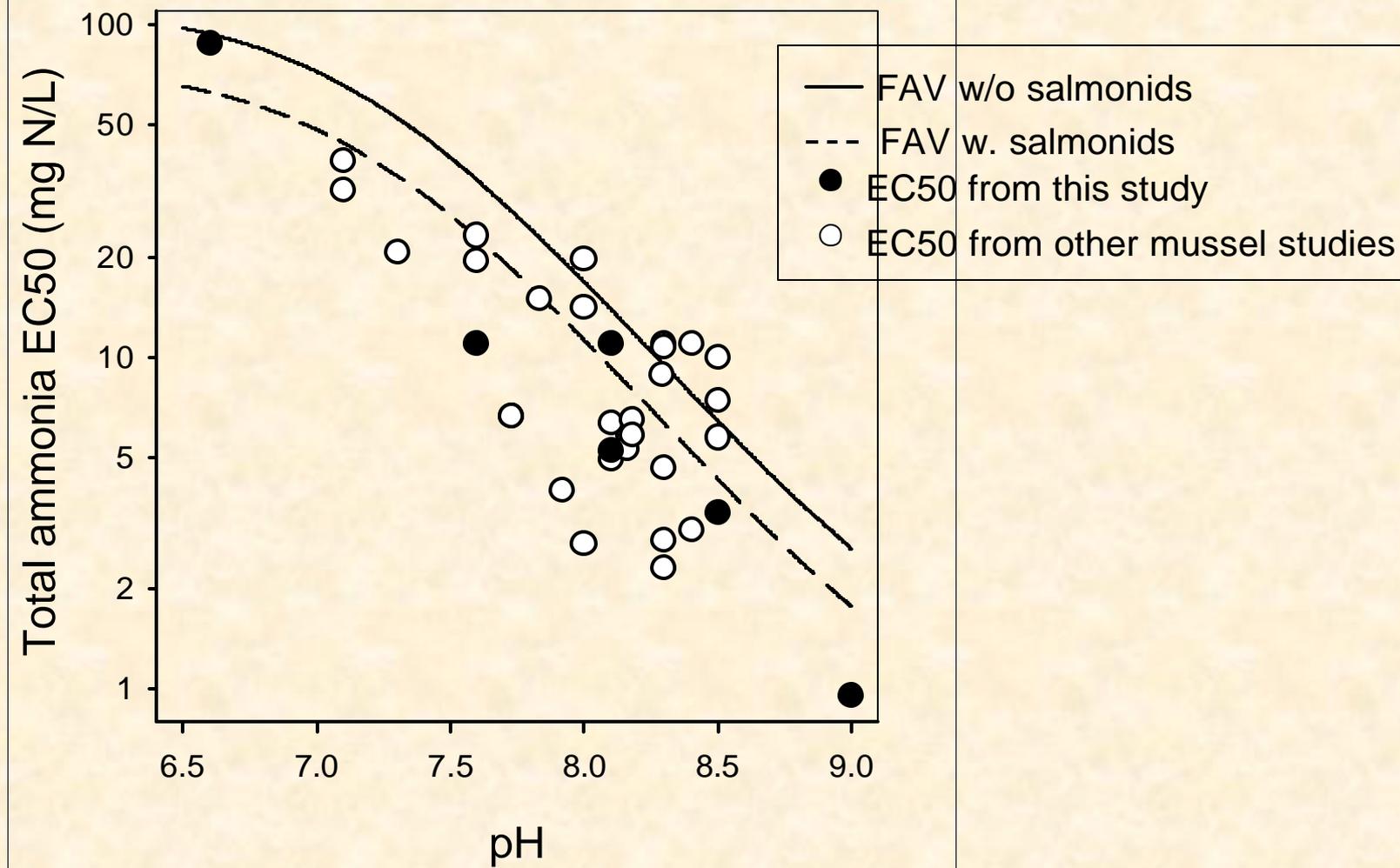


Error bar: 95% confidence interval

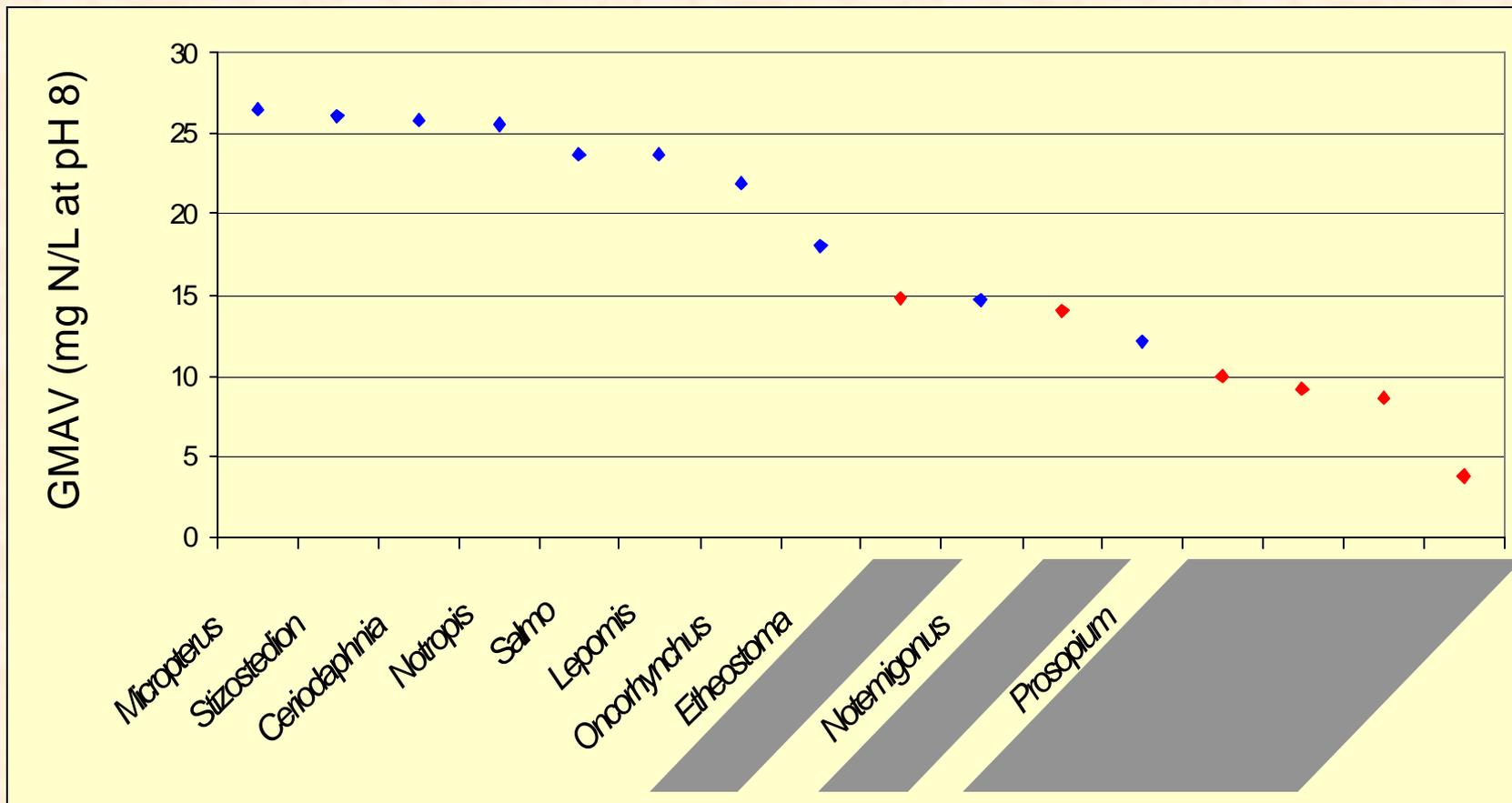
# Ammonia toxicity to juveniles of 11 mussel species in other tests met the ASTM requirements



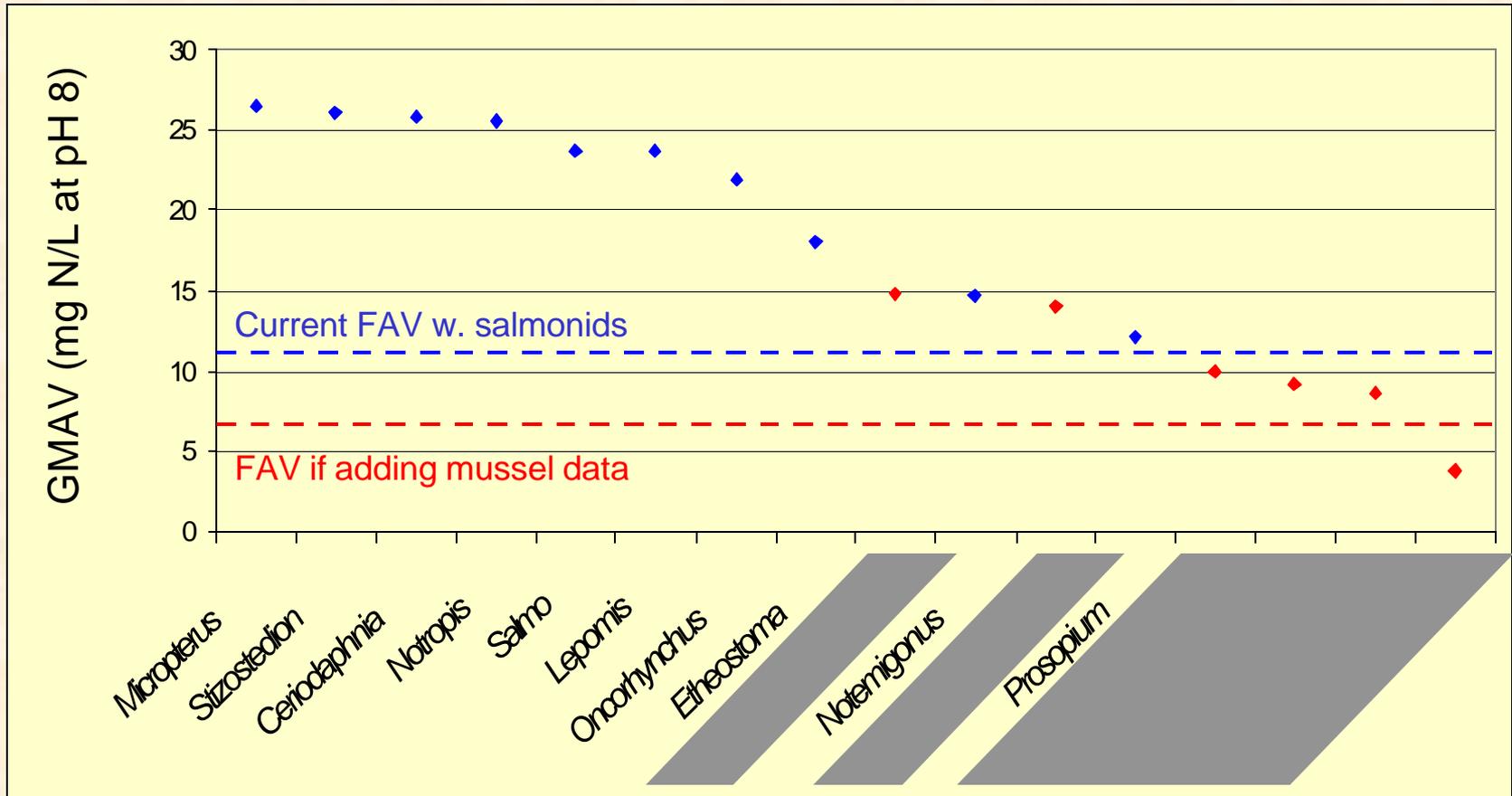
# Comparison of mussel toxicity data to Final Acute Value used to derive EPA water quality criteria (USEPA 1999)



# Ranked GMAVs for ammonia (USEPA 1999), adding data for juvenile mussels (shaded)



# Ranked GMAVs for ammonia and Final Acute Value (USEPA 1999), adding data from juvenile mussels



# Conclusions

## Copper toxicity:

- DOC strongly influenced acute toxicity of copper to juvenile fatmucket
- The BLM in current WQC reliably predicted acute copper toxicity to juvenile fatmucket across a broad range of natural waters
- Adding a small amount of reference natural organic matter to ASTM reconstituted water should be considered for copper toxicity test
- USEPA WQC for copper may not consistently protect fatmucket, and might not adequately protect other mussel species as well

# Conclusions (Continued)

## Ammonia toxicity:

- pH strongly influenced acute toxicity of ammonia to juvenile fatmucket
- Generic relationship of acute ammonia toxicity to pH in WQC for ammonia is appropriate for juvenile fatmucket
- USEPA WQC for ammonia may not adequately protect freshwater mussels